**Supporting Information**

**HYDROVOLTAIC ENERGY HARVESTING FROM NUT SHELLS**

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**Structural and chemical property**

Nutshells contain high amounts of lignin and cellulose, which increase as the nuts mature, with thinner or thicker shells containing similar amounts of lignin contents during shell development. Lignin is primarily located within the corners of the shells rather than the middle.[1] Conversely, cellulose resides within a matrix formed by lignin, while hemicellulose, characterized by its random and amorphous structure, is interwoven with cellulose and occupies the space between cellulose and lignin.[2] This unique arrangement of biopolymers plays a crucial role in the overall properties of nutshells. The chemical treatments can break the internal bonding within lignin and cellulose and thus release more negative surface charge. The negative surface charge of nutshells predominantly arises from the presence of lignin and cellulose, which are abundant constituents of nutshells.[3] Lignin, an amorphous, three-dimensional polymer, is primarily composed of three aromatic monomers, with varying ratios and linkage frequencies depending on the specific nut species. Notably, β-O-4 linkages constitute a substantial portion (40-60%) of the inter-monomeric bonds in lignin.[4] Importantly, lignin features negatively charged groups, with the density of these charges increasing with rising pH levels.[5] In contrast, cellulose is a polysaccharide consisting of repeating glucose units linked by β-glycosidic bonds. Cellulose possesses numerous functional groups, primarily hydroxyl (-OH) groups, with each glucose unit containing three hydroxyl groups. These hydroxyl groups contribute to cellulose's negative charge by interacting with water molecules, leading to the dissociation of hydrogen ions (protons) and the generation of hydroxide ions (OH-), thereby increasing the concentration of negatively charged hydroxide ions in the solution and enhancing cellulose's negative charge. Additionally, the abundance of hydroxyl groups on the cellulose surface facilitates interactions with other charged species, further contributing to its negative charge. The observed surface charge properties of nutshells can be attributed to the dissociation of surface groups, involving deprotonation/protonation reactions at charged sites on the surface, which exist in a dynamic chemical equilibrium. These surface charges play a significant role in electricity generations.

A diagram of a walnut

Description automatically generated

Figure-S 1: WS containing lignin, cellulose and hemicellulose structures.

Table-S 1: Typical Lignin, Cellulose and Hemicellulose contents of four NNS.[6-10]

|  |  |  |  |
| --- | --- | --- | --- |
| **Nutshells** | **Cellulose** | **Hemicellulose** | **Lignin** |
| Almond shells | 38.47 ± 0.39 | 28.82 ± 0.25 | 29.54 ± 0.11 |
| Pecan | 14.5 ± 0.21 | 55.7 ± 0.9 | 29.4 ± 1.0 |
| Walnut shells | 36.38 ± 0.05 | 27.85 ± 0.31 | 43.70 ± 0.57 |
| Filbert Shells | 16 | 18 | 48 |

A graph of different colored bars

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Figure-S 2 : Density of natural nutshells (NNSs) and treated nutshells (NSs)

A close-up of several images of a variety of objects

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Figure-S 3: Cross sections of a) AS, b) FS, c) PS, d) WS.

**A computer model of a house

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Figure-S 4 : 3D drawing of the a) device holder and b) assembled 3D drawing showing the water reservoir and electrode holder.

**Experimental Results:**

**A graph with different colored lines

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Figure-S 5 : Output voltage of four NSs after getting the considerable stabilities at 40 minutes.

A graph of graphing and graphing

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Figure-S 6: a) Analyses of voltage VS time for Platinum and Graphite electrodes; b) Performance analyses of Magnesium (Mg), Titanium (Ti), Platinum (Pt), Graphite (G) electrodes.

To investigate the influence of electrode materials on electrical performance, supplementary experiments utilizing two active metals, titanium (Ti) and magnesium (Mg), were further performed alongside inert electrodes such as platinum (Pt) and graphite (G) as shown in Figure-S 6(b). The Ti-NS-Ti arrangement exhibited little voltage change relative to graphite, suggesting that titanium's influence is akin to that of inert electrodes. The Mg-NS-Mg arrangement exhibited an increased voltage output attributable to galvanic corrosion on the magnesium surface. The corrosion on the magnesium surface because of the water and the hydrovoltaic voltage from the NS structure combindly enhances the device's electrical performance. The improved electrical performance arises from the synergistic effects of hydrovoltaic energy produced by the nutshell structure and the redox processes caused by corrosion on the magnesium surface. The results indicate that the principal source of power in the device is hydrovoltaic energy harvesting, rather than redox reactions at the electrodes, unless galvanic corrosion enhances the output.

**A graph of paper and paper

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Figure-S 7: Output Voltage of WS-H+ and Acid-soaked Paper on the NaOH reservoir.

A close-up of a grey surface

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Figure-S 8: SEM image of the WS sample - submersed on DI water for 7 days

A graph of water and water

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Figure-S 9: FT-IR spectra of de-protonated WS-H+ on NaOH alkaline reservoir.

**A graph and diagram of a wind speed

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Figure-S 10: Effect of a) Wind Speed and b) Light Intensity on the output voltage

The influence of external variables, including wind velocity and light intensity, on the device's electrical performance was meticulously examined. Figure-S 10 (a) illustrates the effect of wind velocity on the voltage output. The TopTes TS-301 Anemometer was utilized to detect wind speed, revealing that an increase in wind speed on the electrode surface corresponded with a rise in voltage output. This improvement is due to increased water evaporation at elevated wind speeds, which enhances the voltage.

To assess the impact of light intensity, the device was positioned under different light settings, with voltage readings recorded following a 15-minute stabilization period. The intensity of light was quantified with a digital illuminance meter. The findings demonstrate that an increase in light intensity proportionately elevated the voltage output, illustrated in Figure- S 10(b). This phenomenon can be attributed to enhanced water evaporation resulting from increased light intensity and heightened surface temperature.

In summary, environmental variables like elevated wind speed, intensified light intensity, higher temperatures, and reduced humidity enhance the device's electrical output. These elements augment water evaporation and boost the overall performance of power generation, hence enhancing the efficiency of the hydrovoltaic system.

A graph of a ph difference

Description automatically generated

Figure-S 11: Output voltage based on the difference in pH values.

Figure-S 11 illustrates the correlation between voltage output and pH fluctuations. An elevated pH gradient produces a greater voltage output; nevertheless, it is important to acknowledge that the device can create substantial voltage even without a pH gradient. An electrical output over 900 mV was documented in the absence of a pH gradient. A more prominent pH gradient results in a higher measured voltage, due to intensified electrochemical interactions. This phenomenon underscores the role of additional elements in overall performance, further affirming that pH is merely one of numerous key impacts on the device's output.

**A graph of a voltage

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Figure-S 12: a) full cycle to reach the stable voltage of dry WS, b) Discharge cycle while drying the wetted WS.

Figure S-12(a) depicts the whole charging cycle to attain and sustain a steady voltage output for the walnut shell (WS) structure. It is observed that achieving maximum voltage in a completely dry WS requires around 6300 seconds, with an initial 2700 seconds necessary for water to completely permeate and reach the upper surface of the WS. The time may vary among samples due to factors like as reservoir water content, evaporation rates influenced by environmental conditions, and the initial drying stage of the WS structure. Upon achieving the stability, the device continue energy generation until the water evaporates completely. Figure S-12(b) illustrates the discharge cycle as the WS structure dries over time. Following a duration of stable voltage generation, the output voltage gradually decreases as a result of the dehydration process. This process is driven by the evaporation from the WS surface. The experiment was performed at room temperature of 25°C and 22% humidity, facilitating natural evaporation. As water evaporates, a notable decrease in voltage is detected after three hours, influenced by environmental conditions for evaporation rates and the residual water on the WS surface.

**Mechanism:**

Because of the pressure differences water droplets traverse the channels persistently and continues to form electrical double layer (EDL) on the path. On contrary, the presence of the EDL augments the pressure drop within a pressure-driven flow.[6] Thickness of the EDL can be determined by using Debye length, shown in **Equation- S 1** which exclusively relies on the concentration of the solution.[7] The charge distribution within the EDL is impacted by the overlapping of the debye length, that eventually affects the streaming potential.[8] The micro/nano channels of NS with varying diameter, affect the extent of Debye length overlap. Larger microchannel surpasses the Debye length, causing similar concentrations of positive and negative ions and constant electrical output along the water flow direction. The electric potential abruptly declines to its bulk value in the deficiency of EDL overlap that leads to homogeneous electric potential distribution.[9] Debeye Length can be expressed as follows [10]:

= **Equation- S 1**

𝞮 is dielectric constant of water, 𝞮**0**is permittivity of vacuum, *k* is Botzmann constant, *T* is Temperature, *e* is the charge of electron, *zi* is valance of the ions, *ci* is the ion concentration.

A specific level of EDL overlap shows maximum efficiency of electric power generation. **Equation- S 1** shows the higher ion concentration will decrease the Debye length. The presence of EDL overlap is very noticeable in concentrated ionic solutions when combined with somewhat concentrated buffers. This has a substantial effect on the structure of the EDL and also affects the time it takes to achieve a stable state. The length of time can be significantly extended, depending on the extent of EDL overlap and determined by factors such as the shape of the channel, NaCl concentrations, the overall acidity or alkalinity, the chemical characteristics of the surface, and the circumstances of the flow. The voltage output of dry NSs is stabilized for a long time because the nanoscale confinement of fluid causes strong interactions between opposing electric double layers (EDLs). In summary, the complicated relationship between EDL overlaps and fluid dynamics highlights the intricacy of generating electric power through pressure-driven nanofluidic flow. Optimal efficiency is reached at precise degrees of EDL overlap. Once a particular amount of saturation is attained, the voltage across the open circuit reaches its peak and remains consistent. This phenomenon occurs as a result of the interaction between the amount of water and the rate of change in ion concentration. At the location where the difference in concentration of ions is greatest, it produces the strongest force that pushes the passage of ions within the micro/nano channels, leading to the maximum streaming potential. Evaporation potential and current can be expressed as per the following equations [11]:

Voc = σνeRsq-preLpre2  **Equation- S 2**

Isc =- **Equation- S 3**

where *σ* denotes the effective charge flux in the precursor, *νe* denotes the evaporating velocity of ethanol in the precursor, *Rsq* pre denotes the square resistance of the precursor, *Lpre* denotes the length of the precursor, and *R* denotes the total resistance.

Nutshells and wood [12] differ significantly in terms of their layout, cell structure, function, and chemical characteristics. Nutshells have a higher density and show better compactness and rigidity because of their delicate lignin content. Nutshells have enhanced surface charge, as well as a greater density of micro/nano channels and unique channel arrangements, rendering them more efficient than wood [13] in generating streaming voltage and current. Further chemical treatments can increase the micro/nano channels of nutshells, thereby enhancing their performance.

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